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# THE CHEMICAL EXAMINATION OF NATURAL BRINES[1]

By O. R. Sweeney and James R. Withrow

The proper analysis of natural brines has always been important. They are used by chemical manufacturers to make comparisons with a view to reaching decisions as to prospective yields of salt, bromine and other products. The war-time elevation of the price of bromine from 30 cents to as high as $6.50 per lb., as well as a similar elevation of other products derived from natural brine, has given rise to search for additional sources of these products and a careful scrutiny of many of the brines encountered in oil, gas and coal development, and hitherto wasted. As a result many analyses have been made in the last three years as a basis for manufacturing consideration. Some of these were made in the laboratories of manufacturers themselves and some by consulting chemists. Analyses from both sources have come into the hands of the authors as the basis for report upon prospective manufacturing values. We, also, have had occasion to make check or confirmatory analyses.

It early became evident that there was no standard or uniform procedure being followed by the different workers. To this fact may be due a large part of the non-agreement encountered from time to time, though inexperience with this type of analysis is also a factor. Few chemists, even water analysts, are experienced in such a type of work as bromine determination in brine. This may be shown best by citing a report to its president by the laboratory of the chemical company. The letter from the president of one chemical company to another stated:

"The analysis of the two samples of brine which you sent us has been completed and it was some job. The results are as follows:

| | Well A | Well B |
|---|---|---|
| Depth | 1200 ft. | 1200 ft. |
| Diameter | 8 in. | 4 in. |
| Specific Gravity of Brine | 1.071 | 1.070 |
| CaO | 0.69 per cent | 0.68 per cent |
| Br | 0.42 | 0.22 |
| Halides (as sodium halide) | 9.21 | 9.26 |
| Iodine | None | None" |

These samples were from a brine whose composition was well known to us. Furthermore, they were on

[1] Read before the Industrial Division, Kansas City Meeting of the American Chemical Society, April 12, 1917.



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the same property. It will be noticed that they are of the same depth and also the same specific gravity, CaO content, and halide content. Nevertheless, they are reported of different bromine content—adivergence of nearly 100 per cent. Such a divergence would be a very important matter industrially, for one of these wells would give nearly twice the yield of bromine for the same turnover of salt and calcium chloride and at the same fuel cost as the other well. Considering the difficulty of bromine determination, by the usual methods, the infrequency of demand for it and the concordance of all other determinations on these two brines one is tempted to suspect the accuracy of the bromine determinations. As a matter of fact even the lower value is over twice the bromine content of the field in question as shown by both analyses by various chemists and experience of *all* the plants operating on this particular brine.

Such situations give rise to controversy and discredit analytical chemistry. An examination of the literature for a basis for standard or uniform procedure disclosed no exact one which could be recommended. The procedures described for the examination of "mineral water" are not applicable directly. Certain modifications which our experience has introduced are recorded here. Not all of the procedures described have been exhaustively studied as yet. The purpose of this paper is to make a beginning with the hope that others, who have had experience in this work, will contribute their experiences, or will criticize these procedures. In this way a procedure may be developed which may be accepted as standard. The object is to develop a method which will meet the needs of the manufacturing chemist rather than a method of exhaustive analysis. Brevity and speed of manipulation, with reasonable accuracy, are, therefore, the requirements.

## ANALYTICAL PROCEDURES

SAMPLE—The sample when pumped from the earth will generally be clear, but on standing it becomes turbid due to the separation of a brown precipitate. This precipitate is mainly iron, but may contain silica and alumina. It is probably caused by oxidation and hydrolysis of ferrous bicarbonate. Generally by the time the sample will have reached the chemist the iron will have separated. The scheme of agitation to suspend the deposit uniformly through the

liquid before taking a part for analysis is inaccurate, as experiments have shown. Furthermore, the specific gravity is changed and this will affect the entire percentage composition. Consideration of this point has led us to conclude that the best procedure would be to collect a sample of about one liter, allow it to oxidize and settle completely, determine the amount of deposit, and then make analyses on the filtered sample. The analysis would not be exactly that of the original brine, but the difference will be very slight, and, since this procedure gives more nearly the thing that the manufacturer wants, it is best to proceed in this manner.

DEPOSIT ON STANDING (AERATION)—The sample of about one liter, which will usually contain some deposit, is allowed to stand, with occasional shaking, and removing of the stopper, for two or three days, or until deposition is complete and the precipitate settles well. The height of the liquid is carefully marked on the outside of the bottle, and the entire sample is then filtered, rejecting the first 100 cc. The precipitate is well washed, ashed and ignited to constant weight. The bottle is dried and the amount of water which it contained to the mark is determined. With these data the grams per liter are calculated, using the specific gravity of the filtered sample, and the result recorded as "*Deposit on Aeration.*" The errors will not be large if percentages be calculated, using this figure. Since in the industries all natural brines are exposed to air and allowed to settle before they are further treated, this value is just what is wanted by the manufacturer. Further examination of the precipitate is not necessary. It is a question whether or not it would be fair to assume the precipitate to be iron oxide ($Fe_2O_3$) and calculate it to, and report it as, ferrous bicarbonate.

SPECIFIC GRAVITY—The specific gravity is obtained by the Westphal balance, and is taken at 15° C., although perhaps it would be better to use 20° C., since this is more nearly the average temperature. The specific gravity of the fresh brine will be different from that of the sample through which the precipitate is suspended, and this in turn will be different from the filtered sample. On one brine, for example, the specific gravity of the filtered sample was 1.2307, while that of the sample in which the precipitate was suspended was 1.2342. If the chemist could take the specific gravity of the clear brine as soon as pumped

from the well it would no doubt be best, from the point of view of the original brine but this will generally be impractical. Even if the specific gravity could be obtained on the fresh brine there would be some volume change after the precipitate settled and a small error would be introduced when taking a filtered sample for later analyses. For these reasons, and also because the manufacturer is interested in the *settled* brine, it is believed that the best procedure is to use the filtered, aerated brine, and to determine the specific gravity with a Westphal balance at 15° C(?). This value is used in calculating percentages.

TOTAL SOLIDS—Many chemists omit this determination because of its questionable accuracy, but its value in calculating total water content for "evaporation fuel" comparisons makes it important. Brines rich in $CaCl_2$ require a rather high temperature, above 160° C., to expel the water completely. At this temperature the magnesium and calcium salts lose a part of their acid constituents, and a wide range of values will be obtained, depending on the temperature and duration of heating. The total solids can be calculated from the complete analysis, but this value should be checked by the total solids as obtained by evaporation. This point is being studied in this laboratory at the present time, and it is hoped that by a suitable arrangement the volatilized acids may be cellected, titrated and then be added to the residual weight of the total solids. It may be that a weighed excess of some base may be added to retain the acid which is otherwise volatilized. The constituents likely to volatilize are chlorine, bromine, iodine (slight), sulfur trioxide and carbon dioxide (slight). The total solids are determined in the filtered sample, using 25-cc. portions and should be reported as *Total Solids by Evaporation*. This gives the manufacturer a basis for a reasonable estimation of the water to be evaporated in working the brine.

SILICA—A 25-cc. portion of the filtered brine is acidulated with 5 cc. of concentrated hydrochloric acid and is evaporated to dryness. It is then dried at 120° C., or higher if necessary, for an hour. Five cc. of hydrochloric acid are then added, the vessel is warmed, 20 cc. of water are added, and, after warming, the whole is filtered and washed free from chlorides. The filtrate is evaporated and treated as just described, and the operation is repeated on the second filtrate. The combined precipitates are ignited in a

platinum crucible, and weighed. The residue is treated with sulfuric and hydrofluoric acids. The loss in weight is reported as *silica*, and the residue is added to the iron and alumina.

IRON AND ALUMINUM—The filtrate and washing, which should contain 5 cc. of concentrated hydrochloric acid, are treated with a few drops of nitric acid, boiled a few minutes, and then made alkaline with ammonia. It is then boiled until all the ammonia is expelled, and after standing, is filtered, washed and ignited in the crucible from which the silica was expelled. The residue is reported as *Iron and Aluminum Oxides*. A separation of the iron and aluminum is not necessary. The results should be reported separately from the iron which separated on aeration. It should be remembered that the iron, aluminum and silica are not in solution as oxides, but as salts. For this reason there will be a slight difference between the total solids on evaporation and the calculated total solids.

Much time is saved if the iron, alumina and silica are all precipitated together, with ammonia. The amount of silica remaining in solution is very small. These constituents have no commercial value, and need not be reported separately. It should be remembered in this latter case that ammonium chloride must be added.

CALCIUM—The filtrate from the iron and aluminum is diluted to 250 cc. and 25 cc. are taken; this is diluted to 150 cc., heated to boiling and a hot 10 per cent solution of ammonium oxalate is added in excess. After standing for some time (15 minutes), it is filtered and washed with hot water. The precipitate is dissolved in warm dilute hydrochloric acid, a little ammonium oxalate solution added, and ammonia then slowly added to complete the precipitation. The precipitate is filtered out, after standing one-half hour, and is ignited to the oxide and weighed, or is dissolved in dilute sulfuric acid and titrated with permanganate. Our experience seemed to show that it was not necessary to allow the precipitate to stand 12 hours as is recommended in some of the books on water analysis. The calcium should be reported as sulfate and chloride.

MAGNESIUM—The combined filtrates and washings from the calcium are acidified with hydrochloric acid, a large excess of sodium hydrogen phosphate is added, and then ammonium hydroxide with constant stirring

until the liquid smells of ammonia. Ten cc. of strong ammonia are added in excess and the whole is allowed to stand 12 hours. The precipitate is filtered out, washed with dilute ammonia and redissolved in hydrochloric acid (1 : 5). The volume is made up to 75 cc., a little sodium hydrogen phosphate added, and then ammonia, drop by drop, with constant stirring until the solution smells strongly. After 4 hours the magnesium is filtered out on an alundum or Gooch crucible, washed with 2 per cent ammonia water, dried and ignited to $Mg_2P_2O_7$. If an alundum crucible is used it should be heated within a glazed crucible. The magnesium should be calculated to the bromide and chloride.

The above procedure gave very good results. In the usual procedure the filtrate from calcium is evaporated to dryness, and the ammonium salts are volatilized. This requires great care, and much time, and did not give any better results than the procedure described. The reprecipitation must be carried out, even on very small amounts. There seems to be good authority, however, for the evaporation and ignition which we have omitted, and the point should be investigated further.[1]

BARIUM AND STRONTIUM—If no sulfates are present, barium and strontium must be looked for. Indeed a case is on record where barium, lead and sulfuric acid were present simultaneously in a natural mineral water.[2] From work in progress in this laboratory it seems, however, that in the case of brines, where very little $CO_2$ is present, that sulfates preclude the presence of barium or strontium. Barium oxalate is sparingly soluble, and a strontium oxalate is insoluble in water. When these metals are present they will be partially precipitated along with the calcium. This point seems to have been overlooked hitherto. In cases where the barium and strontium amount to 0.2 per cent the error introduced cannot be neglected. The magnesium results may also be affected. It may be possible to precipitate the barium and strontium with ammonium sulfate before precipitating the calcium, but no work has been done on this phase. The fact that the barium is not completely precipitated by

[1] In the discussion of this paper in the Industrial Division it was suggested that the speedier method for magnesium, used in Low's "Technical Methods of Ore Analysis," p. 159, might be of service here but we have not yet investigated this method, or the method of precipitation with sodium hydroxide sometimes used on traces of magnesium.

[2] Carles, *Ann. chim. anal.*, **1902**, 91.

ammonium oxalate makes it impossible to apply a correction to the calcium precipitate. The determination of the barium and strontium in the calcium precipitate is too time-consuming to be practical for the ordinary technical analysis. When the barium and strontium content is small the error can be ignored. The procedure used was identical with the one described in the *Department of Agriculturel Bull.*, **91**, "Mineral Waters of the United States," by J. K. Haywood and B. H. Smith; a simpler method has not yet been found.

AMMONIA—Traces of ammonia have been reported in some brines, but the amount is generally so small as to be of no commercial importance. It may be, however, that its significance is greater than we now know, especially in brines for electrolysis. The suggestion has been made by cell operators that nitrogen chloride may be connected with the explosions which occur from time to time in electrolytic chlorine apparatus. If this should prove true the determination of ammonia will be important.

SULFURIC ACID, SODIUM AND POTASSIUM—Fifty cc. of the filtrate from the iron and alumina are diluted to 100 cc. and treated, while boiling hot, with 10 per cent $BaCl_2$ solution, adding it slowly, and with constant stirring. The $BaSO_4$ is filtered off, the paper burned off in a porcelain crucible, and the precipitate dissolved in a few cc. of warm, concentrated sulfuric acid. The solution is now carefully poured into 250 cc. of water, and, after standing some time, is filtered, washed and ignited. It should be reported as calcium sulfate. This method of freeing the $BaSO_4$ from iron and other absorbed matter is very effective. It is essentially that taught for decades at the John Harrison Laboratory, University of Pennsylvania, Philadelphia.

The filtrate from the sulfuric acid is used for sodium and potassium. From this point, the procedure we have been using is the *same* as described in "Mineral Waters in the United States," *Department of Agriculture Bull.*, **91**, *Loc. cit.* It is difficult, however, to determine small amounts of potassium in the presence of large amounts of sodium chloride, and it is believed that some procedure[1] should be used which will precipitate most of the sodium first.

CHLORINE—The brine should be tested with phenol-

[1] Professor C. W. Foulk, of the Division of Analytical Chemistry of the Ohio State University laboratory, is now investigating this matter.

phthalein. It will usually be neutral, but if it is not, it should be made so with $NaHSO_4$ solution. 10 cc. of the filtered sample are diluted to a liter and 10 cc. used for titration. This is diluted to 200 cc., 2 cc. of $K_2CrO_4$ solution are added and the mixture is titrated to the end-point. $Na_2CrO_4$ would probably be a satisfactory indicator here but we have not yet proved this to be true. Take an amount of standard sodium chloride solution equivalent to the amount of silver nitrate used, dilute to 200 cc. and titrate as before. The difference represents the amount necessary to affect the indicator and should be subtracted. This procedure is accurate enough since *the chlorine is used only as a check on the analytical work.* The bromine value must be deducted.

BROMINE—The colorimetric procedure, as given for ordinary waters, is not usable with brines. Experiments showed that after repeated extraction with 90 per cent alcohol the residue still contained bromine. The distillation methods are time-consuming and not very easily manipulated. For these reasons a colorimetric method was developed.

*Procedure*—100 cc. of the brine are made alkaline with $Na_2CO_3$ and are evaporated to dryness. It is then taken up in water and filtered into a 250-cc. flask. It is made distinctly acid with $H_2SO_4$ and is diluted to the mark: 25 cc. are pipetted into a 50-cc. Nessler tube and chlorine is added until the maximum color has developed: 10 cc. of carbon tetrachloride are then added, and the mixture is shaken and compared with a set of standards made up from NaBr solution in the same way. By this rough check the approximate amount of bromine will be discovered, and a set of standard solutions are then prepared which are very close above and below the unknown solution. Again 25 cc. are taken, chlorine water is added to a maximum color and the same amount is added to the standards; the sample is then shaken with 10 cc. of $CCl_4$ and poured into a wet filter; when the water has drained off the filter should be punctured and the liquid caught in a 25-cc. Nessler tube (this is best done in a darkened room but darkness is not essential). If a sample does not exactly match the standard the colors can be compared by diluting with $CCl_4$; or since the operation is so simple, a new set of standards can be made up, and then a new determination made. If a test shows that all bromine was not extracted by

10 cc. of $CCl_4$ a second extraction should be made. This is generally not necessary.

Traces of iodine which are present in most brines will not interfere. The iodine need not be reported.

It is difficult to appreciate the unreliability of published statements regarding the occurrence of bromine. For instance, although the State of Michigan reports, and the most reliable information states, that Midland, Mich., brine contains 0.1 per cent of bromine, yet the most exhaustive German work on bromine[1] states on page 3 that the brine from Midland, Ohio, *sic.*, contains 4.18 per cent magnesium bromide which is equivalent to 3.63 per cent bromine, or 36 times stronger than those who operate on it claim it to be.

## REPORTING RESULTS

The results should be reported in such a manner as to give the manufacturer the thing which he wants. The reporting of the constituents as ions, while strictly scientific, is of no value to the manufacturer. All of the sodium and potassium should be calculated to chloride. Since the $CaSO_4$ separates on the copper tubes in the evaporators the $H_2SO_4$ should be reported as calcium sulfate. The bromine should be calculated as magnesium bromide, since it has long been so considered in the trade; but bromine as free bromine should also be reported. The residual calcium and all the magnesium are calculated to chlorides since they go on the market as such. Strontium and barium should be given as chlorides. The silicon should be reported as the oxide since the form in which it is combined is not known. Iron and aluminum are reported together as oxides since their separation is too time-consuming. The residue which separates on standing should also be given. Results are preferably reported in percentages though some manufacturers are accustomed to *grams per liter*. The specific gravity and temperature should always be reported; for this reason also, a standard temperature should be used so that results would be really comparable.

When the positive and negative ions are calculated to compounds they should nearly satisfy each other. It should be borne in mind, however, that the iron, aluminum and silicon are given as oxides, and not as salts, in which form they usually occur in the brine.

[1] "Monographien ü. angewandte Electrochemie. Über d. elektrolytische Gewinnung von Brom," by Max Schlötter.

There may also be small amounts of $CO_2$ and iodine which are not included. If, however, the check is not reasonably close, it indicates an error, or else some undetermined constituent is present.

As an illustration of the extremes in composition which the analyst must expect to meet, two examples from Ohio brines will serve.

| Brine Source: | Eastern Ohio Coal Mine | Southern Ohio Driven Well |
|---|---|---|
| Specific gravity | 1.034 | 1.180 |
| Baumé equivalent | 4.8° | 22.2° |
| Sodium chloride | 3.26 per cent | 12.08 per cent |
| Magnesium bromide | 0.007 | 0.124 |
| Bromine | 0.006 | 0.107 |
| Calcium chloride | 1.63 | 10.81 |
| Magnesium chloride | 0.05 | 2.61 |
| Calcium sulfate | 0.001 | 0.03 |
| Iron and aluminum oxides | 0.21 | 0.04 |
| Silica | 0.12 | 0.002 |
| Residue on evaporation | 5.23 | 29.00 |

While this work considers primarily the commercial natural brines, the same procedure will doubtless apply to the analysis of artificial brines, such as used in soda ash manufacture and in electrolytic cells, although the amounts of calcium and magnesium will be much less in these solutions.

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